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CHEMICALLY POLISHED QUARTZ.

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18. SUPPLEMENTARY NOTES

This report is a slightly modified version of the report which appeared in the Proceedings of the 31st Annual Symposium on Frequency Control, June 1977.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

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Lapping	Cultured Quartz	Chemical Polishing
Polishing	Etched Crystals	Ammonium Bifluoride
Etch Pits		

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)
Etching in a saturated solution of ammonium bifluoride is shown to be capable of producing chemically polished AT-cut quartz surfaces over a broad range of conditions. The quality of chemical polish depends primarily on the surface finish prior to etching, the depth of etch and the quality of quartz used. The speed of polishing depends primarily on the temperature of the etching bath. In an 88 degree C etching bath, starting with 3 micrometers lapped blanks, chemically polished blanks with a surface roughness of 0.1 micrometer and a roughness

20. ABSTRACT (continued)

angle of 1 degree can be produced in 15 minutes. Starting with a finer surface finish can produce a smoother chemically polished surface.

Chemically polished blanks are shown to be extremely strong. Fundamental mode 20 MHz resonators made with chemically polished natural quartz blanks showed no Q degradation with increasing depth of etch.

Of sixteen different varieties of cultured quartz from ten different growers, most were found not to be suitable for chemical polishing because of a large number of etch channels generated by the etching. The incidence of channels varied greatly from cultured quartz to cultured quartz. A vacuum-swept cultured quartz was the only variety from which chemical polishing could produce blanks free of etch channels. Of a large number of 6.4 mm diameter chemically polished natural quartz blanks, approximately two-thirds were free of etch channels.

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INTRODUCTION

High precision and high frequency quartz resonators, particularly those for high shock applications, require quartz plates whose surfaces are free of imperfections, such as scratches and pits. The most common method of achieving such surfaces is mechanical polishing. The mechanical polishing processes are difficult to control (i.e., it is difficult to produce defect-free surfaces, at the correct frequency, with a high yield). Moreover, as has been known since the last century, even when the polished surfaces appear to be free of defects when examined at high magnification, the surfaces contain hidden defects.[1,2] These defects can be revealed by X-ray diffraction topography[3] and by etching subsequent to polishing.

Figure 1 is an SEM micrograph which shows the two most commonly observed defects revealed by etching polished quartz blanks: scratch marks and pits. As we shall discuss later, the pits often extend deep into the blanks.

The objective of the study to be described in this report was to overcome the difficulties associated with mechanical polishing by finding an etching procedure capable of producing chemically polished quartz crystal surfaces.

CHEMICAL POLISHING

At the beginning of this study, a literature search was conducted to determine what previous studies, if any, have been reported on the subject of polishing quartz chemically. No such reports were found. Perhaps, this is due to the fact that it has been widely known that the etch rates of quartz vary greatly with crystallographic direction.[4,5] The rate along the fastest etch direction, the Z direction, is over one hundred times the rate along the slowest etch direction, which is the -X direction for right-handed quartz. At first glance, therefore, achieving a chemically polished quartz surface may seem like a hopeless task.

It has, however, been shown that other highly anisotropic materials, such as silicon and germanium, can be polished chemically.[6] To understand why such anisotropic materials can be so polished, let us examine the etching mechanism.

1. Rabinowitz, E., "Polishing," Scientific American, Vol. 218, pp. 91-99, June 1968.

2. Holland, L., "The Properties of Glass Surfaces," London: Chapman and Hall, Chapter 1 (1964).

3. Newkirk, J. B., Young, J. D., and Spencer, J. P., "Defect Structures on Polished Quartz Surfaces as Seen by X-ray Diffraction Microscopy," J. Appl. Phys. Vol. 35, pp. 1362-1363 (1964).

4. Frondel, C., "The System of Mineralogy ...," Vol. III, Silica Minerals, New York and London: John Wiley and Sons, Inc., pp. 162-163 (1962).

5. Ernsberger, F. M., "Structural Effects in the Chemical Reactivity of Silica and Silicates," J. Phys. Chem. Solids, Vol. 13, pp. 347-351 (1960).

6. Holmes, F. J., "The Electrochemistry of Semiconductors," London and New York: Academic Press, Chapters 6 and 8 (1962).
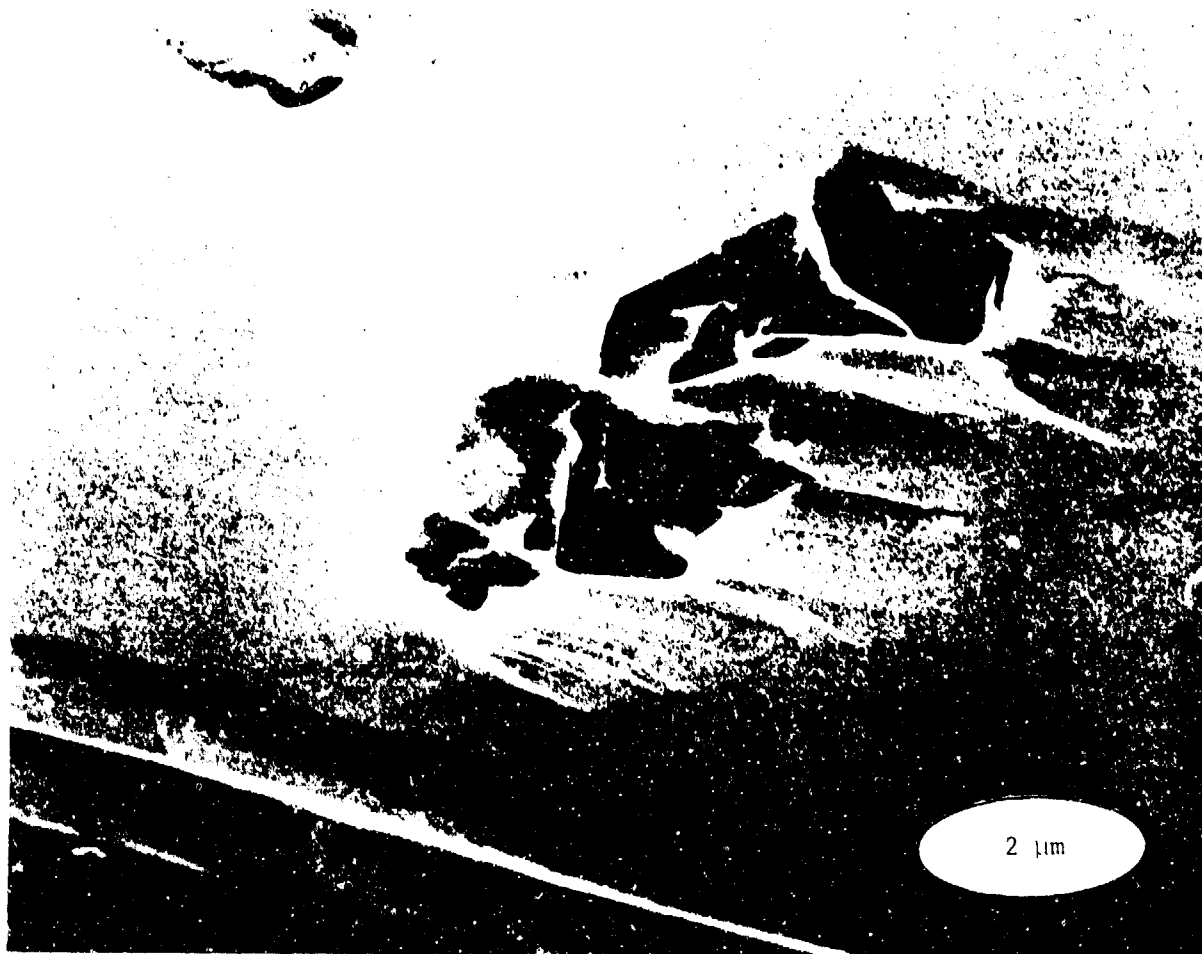
Figure 1. Polished Surface after Etching.

Etching can be considered to be a five-step process. The etchant must:

1. diffuse to the surface,
2. be adsorbed,
3. react chemically;

the reaction products must:

4. be desorbed, and
5. diffuse away from the surface.

The etching rate may be limited by any one of these steps. In chemical polishing, the rate controlling step is generally the diffusion to or from the surface. Diffusion control means that, in particular, the inherent rate at which a reaction takes place at the surface is higher than the rate of diffusion; i.e., the etchant molecules at the surface react at a rate which is faster than the rate at which the concentration at the surface can be

replenished by the diffusion of other etchant molecules. A depleted surface layer therefore exists, outside which the etchant concentration is uniform, but inside which the concentration decreases to near zero at the surface.

Under such conditions, the etching is principally determined, not by the properties of the surface being etched, but by the diffusion. It is clear that if a surface initially consists of hills and valleys, as shown in Figure 2, the probability of an etchant molecule diffusing to the top of a hill will be much greater than the probability of its diffusing to the bottom of a valley. The hills will therefore be etched faster than the valleys, and the surface will become increasingly smooth as the etching progresses.
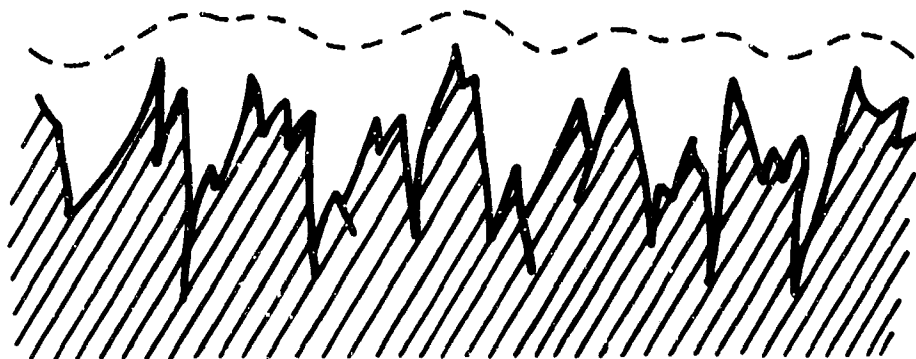
Figure 2. A Rough Surface at the Beginning of Etching.

Eventually, the surface becomes so smooth that the depleted layer can have uniform thickness everywhere, e.g., as shown in Figure 3. From that point, the surface is etched evenly everywhere, and the surface smoothness no longer improves with further etching. Chemically polished surfaces are therefore not perfectly flat but are microscopically undulating.
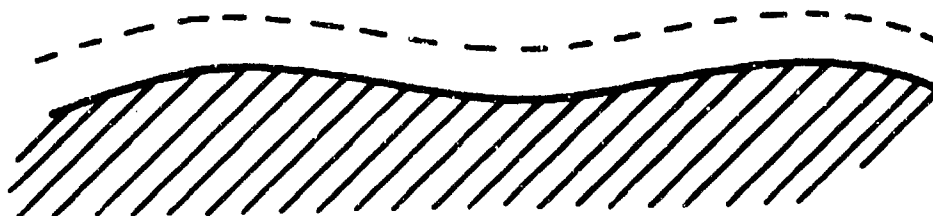
Figure 3. Chemically Polished Surface.

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ETCHING EXPERIMENTS

Not enough information exists at the present time for one to be able to predict the conditions under which a given etchant can chemically polish quartz. At the beginning of this study, an empirical evaluation of a number of the known etchants for quartz was planned. The evaluation began with ammonium bifluoride ($NH_4F \cdot HF$), simply because that had been the etchant used in our fabrication process and was therefore the most readily available. As it turned out, we need not have looked any further.

Most of the experiments were performed on AT-cut plano-plano natural quartz blanks which had been final lapped with 3 μm MICROGRIT aluminum oxide abrasive[7] and then etched under various conditions in increments up to $\Delta f = 160 \, f_o f_f$, where Δf is the change in frequency in kHz, and f_o and f_f are the initial and final frequencies, respectively, in MHz. In the past, the depth of etch has usually been expressed in units of f^2 because the depths of etch normally used in crystal fabrication have been small enough so that it did not matter if f meant f_o or f_f. For the deep etches evaluated in these experiments, the proper unit is $f_o f_f$. (Since $t_o \propto \dfrac{1}{f_o}$ and $t_f \propto \dfrac{1}{f_f}$, $\Delta t \propto \dfrac{\Delta f}{f_o f_f}$.)

For AT-cut quartz, $1 f_o f_f = 1.66$ μm removed from the thickness.

SURFACE EVALUATION

The etched blanks were first inspected with a light microscope to assure that no gross defects were present. The blanks were then examined with a scanning electron microscope (SEM) and with a Talysurf profile meter.[8]

The topography of deeply etched AT-cut quartz surfaces consists of hills and valleys which extend in a direction about 4° from the X axis. Therefore, in both the SEM and profile meter measurements, the topography appears smoothest when examined along a direction parallel to the hills and valleys, and appears roughest when examined perpendicular to the hills and valleys. Figure 4 shows SEM micrographs of the same surface taken from the two different angles. These SEM micrographs, as well as all the others in this report were taken along an observation angle of 60° from the normal in order to provide good contrast and resolution. The micrograph on the left was taken looking along the hills and valleys; the micrograph on the right was taken looking across the hills and valleys. The scale is represented by an oval because of the oblique observation angle used.

Similarly, Figure 5 shows profile meter scans for the same surface along the two orthogonal directions. The profile meter is a stylus type instrument, similar to a phonograph. A very fine diamond needle is moved across the surface. The up and down displacements of the needle are converted to an electrical signal which is displayed on a chart. Since the depths of the valleys were generally small compared to the separations of the hills, the vertical scale in this example is magnified 200 times as compared to the horizontal scale. The surface appears roughest along the Z direction,

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7. Micro Abrasives Corp., 720 Southampton Rd., Westfield, MA 01085.

8. Talysurf 4, The Rank Organisation, Rank Taylor Hobson, Leicester, England.
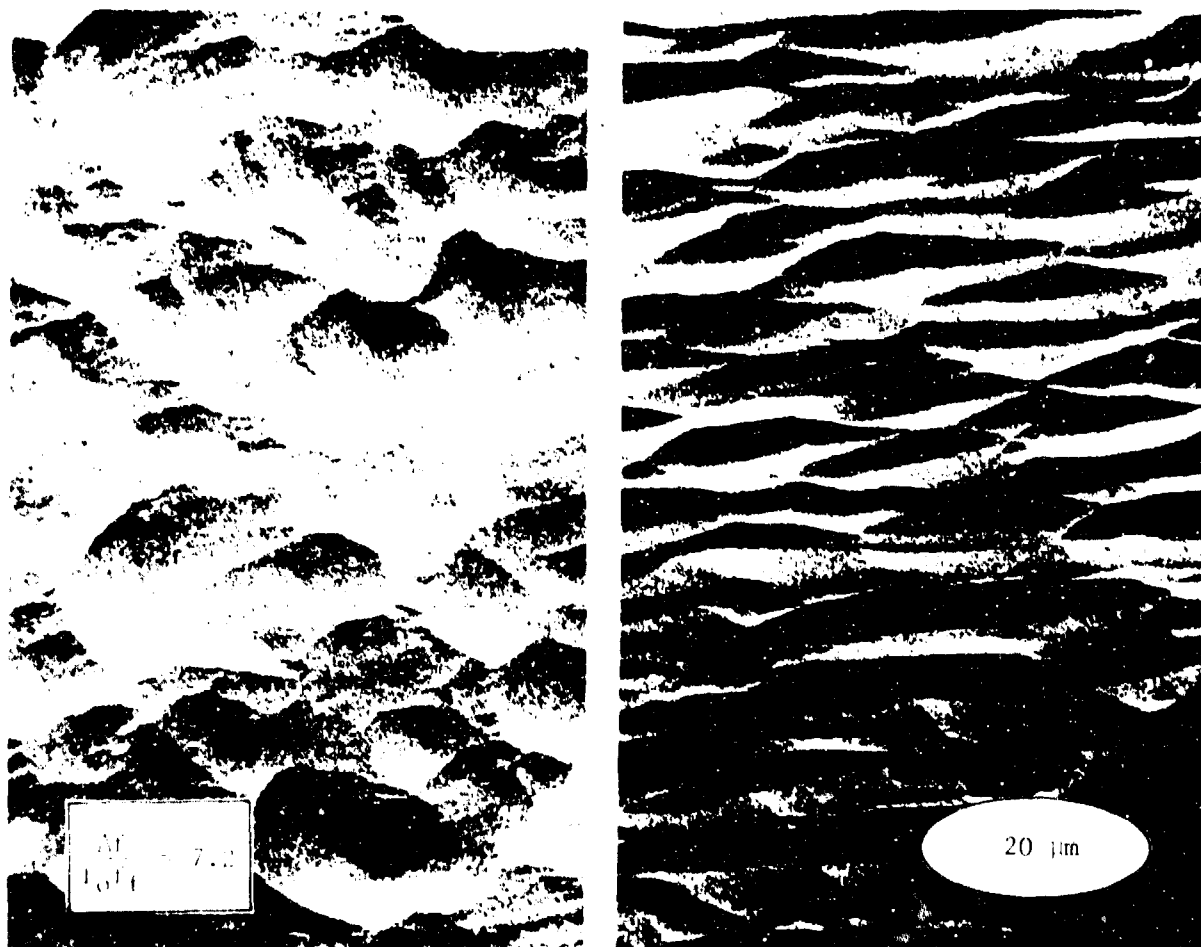
Figure 4.   SEM Micrographs of the Same Surface from
Two Different Observation Angles.

i.e., the direction where the needle is moving perpendicular to the hills and
valleys. It is, therefore, this direction on which all calculations of sur-
face roughness in this report are based.

The Z direction profile meter scans were digitized,[9] and from this data
the surface topography was characterized for each sample by two parameters:
the surface roughness and the roughness angle. The surface roughness was
derived by calculating the root mean square deviation from an imaginary,
smooth "zero spacially averaged" line which is chosen so that the area of
mountains above this line is equal to the area of valleys under this line.
The roughness angle is the average angle which the sides of the hills make
with the plane of the crystal blank.

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9. Model 9869A Digitizer with a 9820A Calculator, Hewlett-Packar⊦ Co.,
Palo Alto, CA   94303.
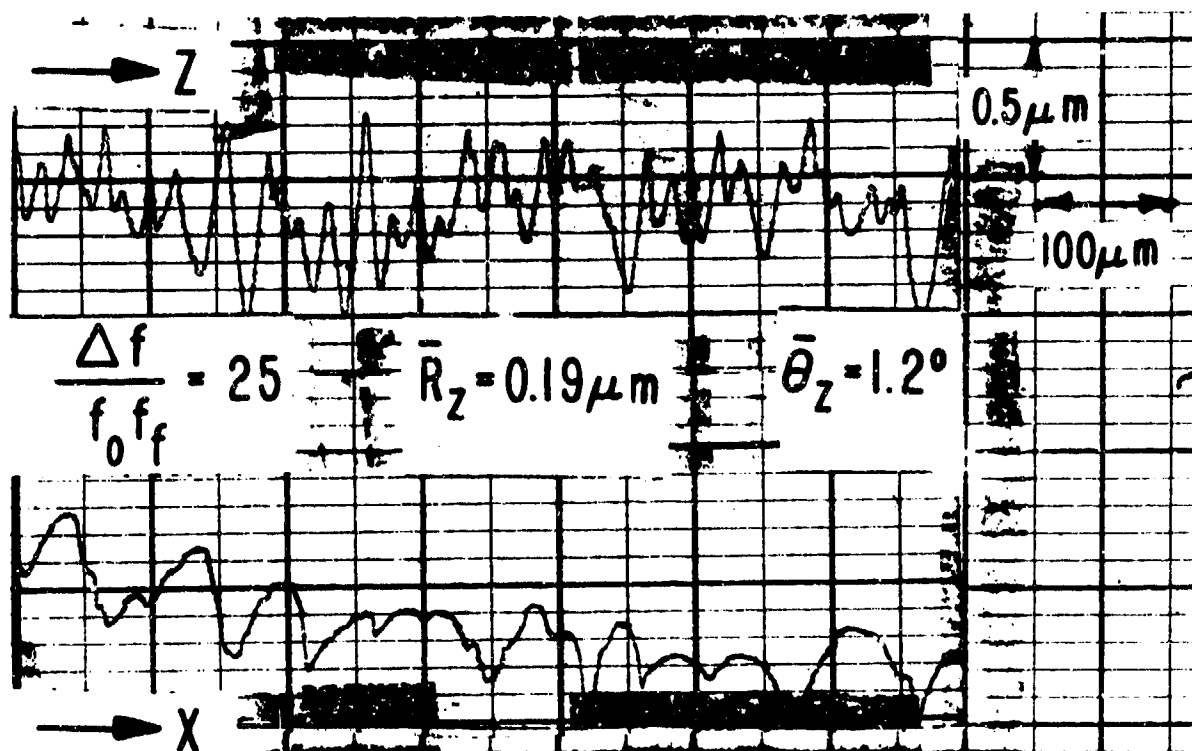
Figure 5. Profile Meter Scans of the Same Surface along Two Orthogonal Directions.

Etching Apparatus

The etching experiments were performed in the double beaker arrangement shown in Figure 6. A 1000 ml glass outer beaker contains water and a floating 400 ml Teflon beaker,[10] which in turn contains the saturated ammonium bifluoride solution. A temperature controlled stirring hot plate with a thermistor sensor[11] was used to control the temperature of the water surrounding the Teflon beaker. The temperature of the ammonium bifluoride solution could thus be controlled to about $\pm 1.5^\circ$C. A thick Teflon disc with a diameter slightly larger than the outer beaker was used as a cover to minimize evaporation from the beakers. The weight of this disc also served to push the inner beaker down to assure that the fluid level in the inner beaker was always about 3 cm below the water level in the outer beaker. A hole through the center of the disc permitted the agitation of crystals during etching.

Since the thermal conductivity of the Teflon beaker is low, to minimize the time required for the temperature of the inner bath to reach equilibrium with the outer bath when the hot plate was first turned on, the inner bath was preheated in boiling water in a separate container. Even with this method

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10. Model No. J40, Fluoroware, Inc., Jonathan Industrial Center, Chaska, MN 55318.

11. Model No. 4812, Cole Parmer Co., 7425 N. Oak Park Ave., Chicago, IL 60648.

Figure 6. Etching Apparatus

It took well over an hour after the hot plate was turned on for the inner
bath to stabilize at 85°C, for example. In production, it may be preferable
to use direct heating of the solution by means of an alumina or Teflon-coated
immersion heater.

The crystals were held in a Teflon jig which was designed to assure that only point contacts existed between the jig and the crystals. For crystals with a diameter greater than 16 mm, a commercially available jig[12] was found to be adequate. For the smaller crystals used throughout most of our experiments, a small "home made" Teflon jig was used, which fit on the same Teflon handle as the commercial device. The crystals were agitated slowly in both directions by means of a constant-speed electric motor, a (now obsolete) Hewlett-Packard Model 297A Sweep Drive. During most of the experiments, the motor was set to rotate the etching jig through an angle of approximately 360° before reversing direction. The rate of agitation was about 5 cycles per minute.

Etching Procedure

The etching procedure consists of the following steps:

1. A saturated solution of ammonium bifluoride is prepared in a Teflon container. The ammonium bifluoride ($NH_4F \cdot HF$) flakes[13] are mixed with distilled water, and the solution is heated to the desired temperature. The amount of $NH_4F \cdot HF$ used is such that after the solution reaches the equilibrium temperature, some undissolved flakes remain in the bottom of the container throughout the etching process. (The solubility of $NH_4F \cdot HF$ in water increases from 61 grams per 100 ml of solution at 60°C to 86 grams per 100 ml at 100°C.[14]) The solution preparation and the etching are performed under a vented hood to prevent inhalation of the vapors from the etching bath.

2. The crystals are cleaned thoroughly. To assure that the surfaces are etched evenly, it is particularly important to remove all contaminants such as waxes and greases, which may be impervious to the etchant. The crystals used in these experiments were thoroughly degreased by a process which included the immersion of the blanks in ethyl alcohol in a Petri dish whose bottom was lined with open-cell urethane foam. Both sides of each blank were scrubbed with a foam swab. The crystals were then placed into the slots in the etching jig and agitated ultrasonically in a detergent solution and rinsed thoroughly. Plasma cleaning in an oxygen plasma[15] has been found to be a reliable alternative to scrubbing.

3. From the final rinse the crystals are transferred, while wet, into the etching bath and are jiggled around to make sure that there are no trapped air bubbles in the etching jig. During etching, the crystals are agitated in both directions to assure even etching on both sides. The approximate etching time can be calculated from the etching rate vs. temperature curve of Figure 7, which will be discussed later. A table such as the one in Appendix A can be used to facilitate the etching to frequency.

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12. Model No. A14-01, Fluoroware, Inc., Chaska, MN 55318.

13. Catalog No. A-664, Fisher Scientific Co., Fair Lawn, NJ 07410. (Also obtained the same results with Catalog No. 0618, J. T. Baker Chemical Co., Phillipsburg, NJ 08865.)

14. "Guide to Physical Properties of J. T. Baker Industrial Inorganic Chemicals," J. T. Baker Chemical Co., Phillipsburg, NJ 08865.

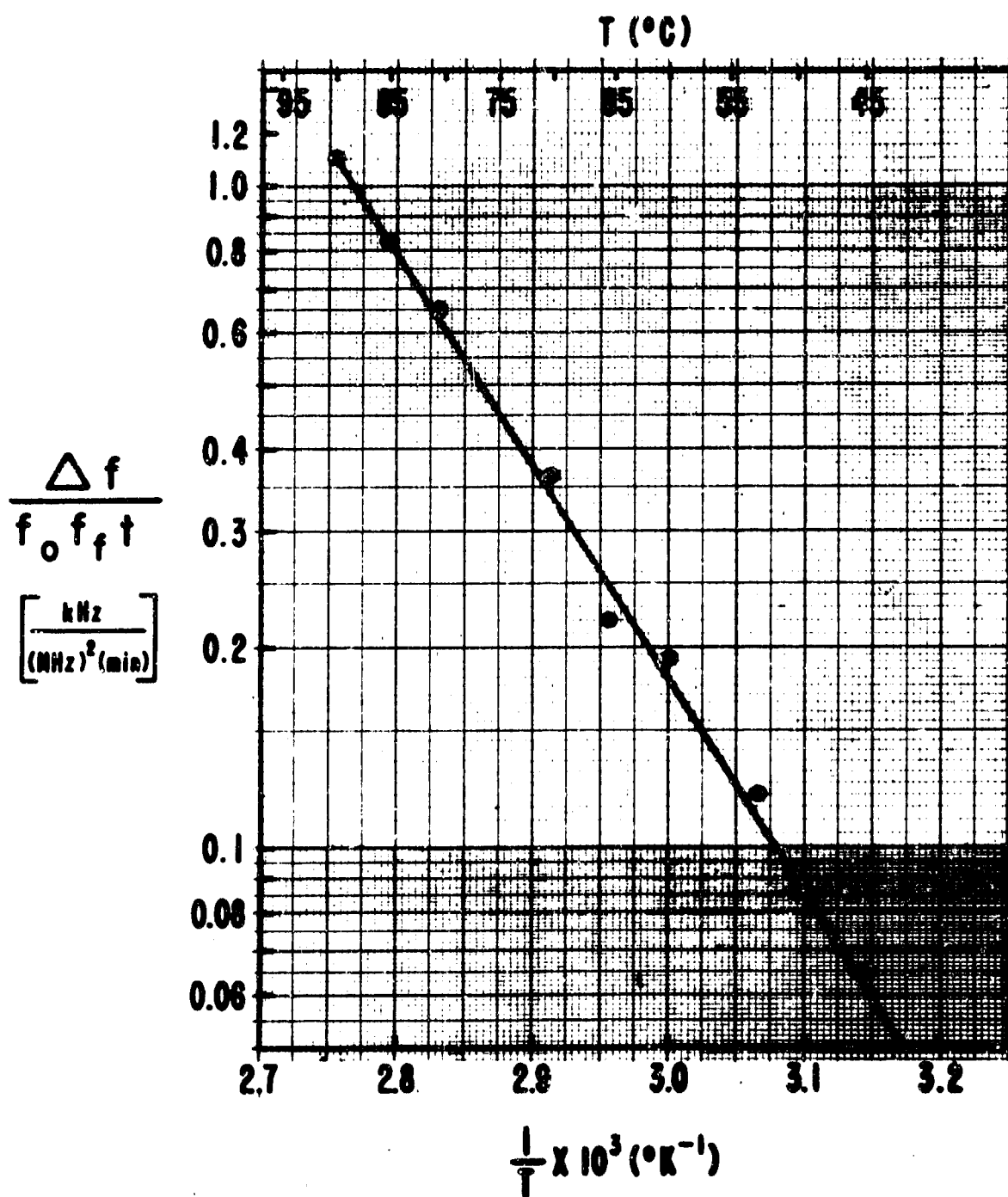15. Plasmod model, Tegal Corp., 860 Wharf St., Richmond, CA 94804.

Figure 7. Temperature Dependence of Etching Rate.

9

4. After the crystals reach the desired frequency, the etching jig is removed rapidly from the etch bath and is immersed immediately into a container of hot water, then given a thorough rinse under running hot water, then agitated ultrasonically in hot water, then given another rinse in running distilled water, then dried by spin drying. A thorough rinse is important in order to remove all residues of the etchant.

5. The crystals are then inspected under a microscope for uniformity of etch and for defects such as scratch marks, etch pits, and etch channels.

Non-uniform appearance of the etched surfaces can have the following causes: (a) contamination on the crystals prior to etching, (b) contamination in the etch bath which adsorbs onto the crystals, (c) air bubbles on the crystals which remain after the crystals are immersed in the etch bath, (d) contact between the crystals and the etching jig due to poor jig design or inadequate agitation, (e) poor quality quartz in which a large number of etch pits and etch channels are produced by the etching, and (f) inadequate rinsing at the completion of etching.

Silicon dioxide surfaces on oxidized silicon slices have been shown to retain fluorides even after a 2-minute rinse in 95°C water.[16] The authors of this report ascribe the "tenacious behavior of the fluoride ion . . . to the strength of the silicon-fluoride bond (136 kcal/mol compared to 106 kcal/mol for Si-O) on the . . . SiO_2 surface." However, a careful analysis by Auger Electron Spectroscopy of several of our etched quartz blanks which had been rinsed thoroughly with distilled water failed to reveal any traces of fluorine on the surfaces. (To minimize the possibility of electron beam-induced desorption of the fluorine, the samples were translated across the primary beam continuously while repeatedly scanning a narrow range of energies about the fluorine peak.)

Inspection Procedure

The inspection of etched blanks is performed under a microscope at about 40 X magnification using a black background with the light incidence perpendicular to the axis of the microscope. First, the crystal is inspected for surface irregularities such as scratch marks, pits, and twinned areas by tilting the crystal so as to reflect light into the microscope. The crystal is then inspected for etch channels by holding it so that the light incidence is in the plane of the crystal (i.e., edge illumination). The etch channels are most visible when the edge illumination is incident along a direction perpendicular to the direction of the channels. For example, in most cultured quartz, the etch channels tend to be along directions near the Z direction. These channels are most easily visible, therefore, with a light incident from the X direction. To help make the etch channels more visible without rotating the crystals, it is helpful to use for the edge illumination two lights incident at a right angle to each other, or a ring light. The etch channels appear as small, bright streaks which extend through the blank from one side to the other. The thicker the blank, the longer the streaks; and the deeper the blank has been etched, the brighter the streaks.

16. Larrabee, G. B., Heinen, K. G., and Harrel, S. A., "Measurement of the Retention of Fluoride by Silicon and Silicon Dioxide Surfaces," J. Electrochem. Soc., Vol. 114, pp. 867-869, August 1967.

Etching Variables

The etching variables investigated in this study were: the depth of etch, the surface finish prior to etching, the etching temperature, agitation during etching, etching bath depletion, and the quality of quartz used.

a. <u>Depth of etch</u>: Figure 8 shows an SEM micrograph of the 3 μm alumina lapped surface prior to etching. The surface is filled with pits, crevices, and loose and nearly loose particles. After etching to $\Delta f = 1.5f_o f_f$, the loose and nearly loose particles have been etched away, as shown in Figure 9; however, numerous pits remain visible. A surface etched to $\Delta f = 2.1f_o f_f$, in Figure 10, shows fewer pits. The pits have become broader and shallower.

Figure 11 shows the topography corresponding to a depth of etch of $\Delta f = 3.6 f_o f_f$. Evidence of the surface damage produced by lapping has nearly disappeared. The hills and valleys, which tend to extend along about the X direction, have become more apparent. The surface roughness at this point is 0.19 μm, and the roughness angle is 4.0^o.

As the etching progresses, the hills move further apart, and the valleys become shallower. Figures 12 and 13 show the topographies corresponding to depths of etch of $\Delta f = 8.9f_o f_f$ and $\Delta f = 31.5f_o f_f$. The surface roughnesses and roughness angles are 0.13 μm and 2.8^o, and 0.09 μm and 0.7^o, respectively.

Upon further etching, the topography changes less and less with increasing depth of etch. The surface roughnesses and roughness angles approach the equilibrium values of 0.075 μm and 0.25^o, respectively. Beyond a depth of etch of $\Delta f \simeq 80f_o f_f$, the topography no longer changes with increasing depth of etch. Figure 14 shows an SEM micrograph for a surface etched to $\Delta f \simeq 85f_o f_f$.

The effect of the hills and valleys on the surface areas of these chemically polished blanks is small. For example, at a depth of etch of $\Delta f \simeq 25f_o f_f$, the ratio of surface areas between chemically polished blanks and "perfectly" polished blanks is less than 0.01%.

b. <u>Surface finish prior to etching</u>: Four groups of crystal blanks, each with a different surface finish prior to etching, were etched at 85°C. The surface roughness and roughness angle vs. depth of etch was determined for each group. The four groups were prepared as follows: one group was cut with a diamond saw blade (80 grit) and was not lapped at all; the second group was final lapped with 12 μm MICROGRIT aluminum oxide abrasive; the third group was final lapped with 3 μm MICROGRIT; and the fourth group was lapped with 3 μm MICROGRIT, etched, then polished with cerium oxide.

The surface roughnesses and roughness angles of the blanks with the diamond saw blade surface finish continued to decrease, with little sign of leveling off, all the way to a depth of etch of $\Delta f = 300 f_o f_f$, the maximum depth to which this group was etched. The surface roughnesses and roughness angles decreased nearly linearly from 3.0 μm and 3.6^o, respectively, at $\Delta f = 110f_o f_f$, to 1.2 μm and 0.9^o at $\Delta f = 300f_o f_f$. As the etching progressed, the blanks became more and more transparent.

Figure 8.   Unetched 3 μm Lapped Surface.

12
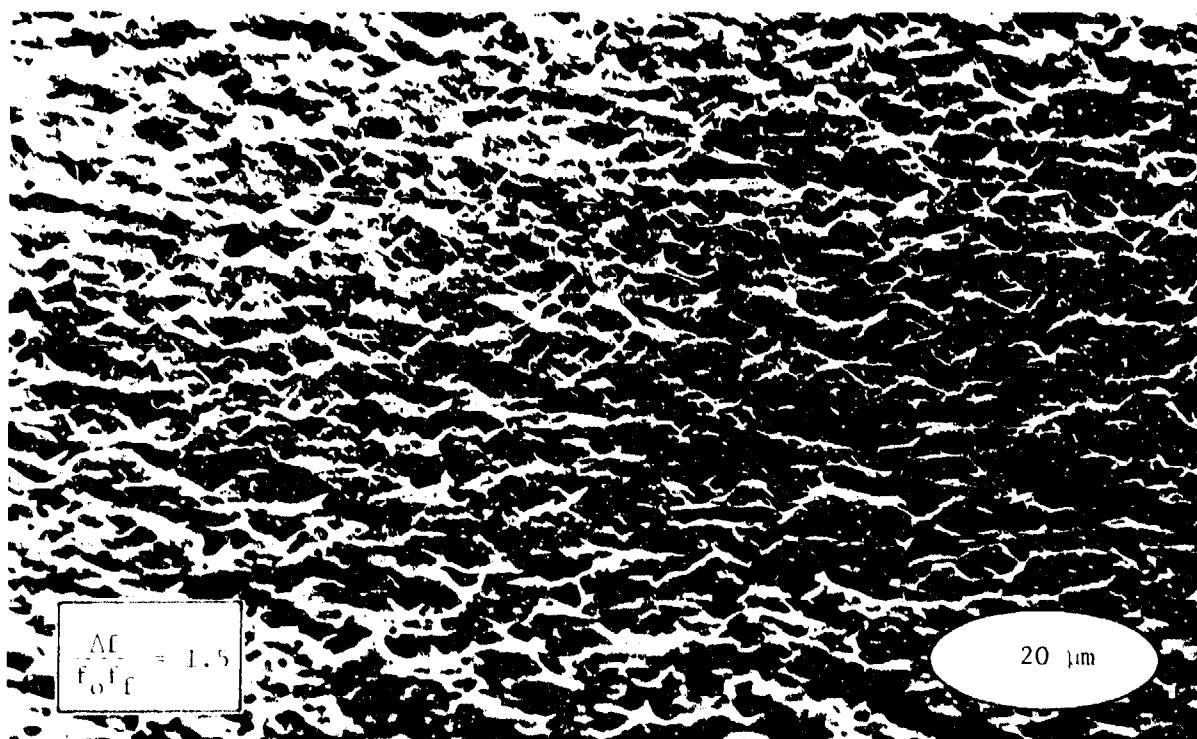
Figure 9.   Surface Etched to $\Delta f = 1.5 f_o f_f$.
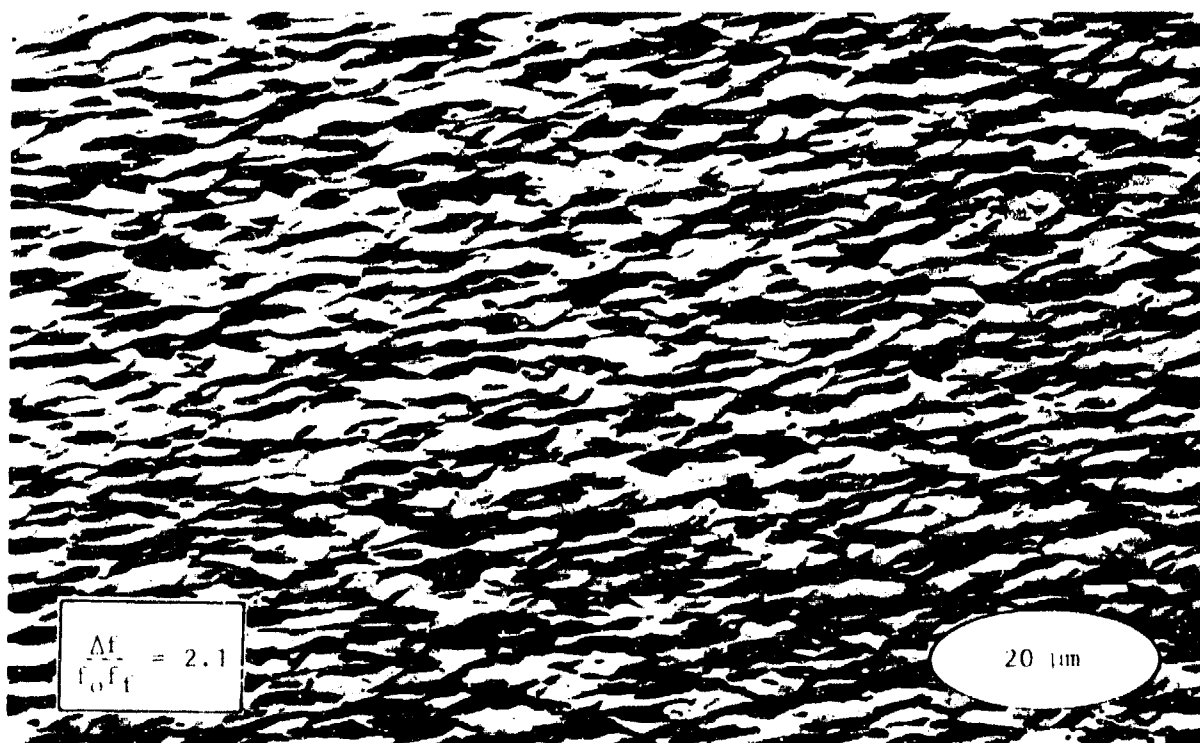
Figure 10.   Surface Etched to $\Delta f = 2.1 f_o f_f$.

$$\frac{\Delta f}{f_o f_f} = 3.6$$

20 μm
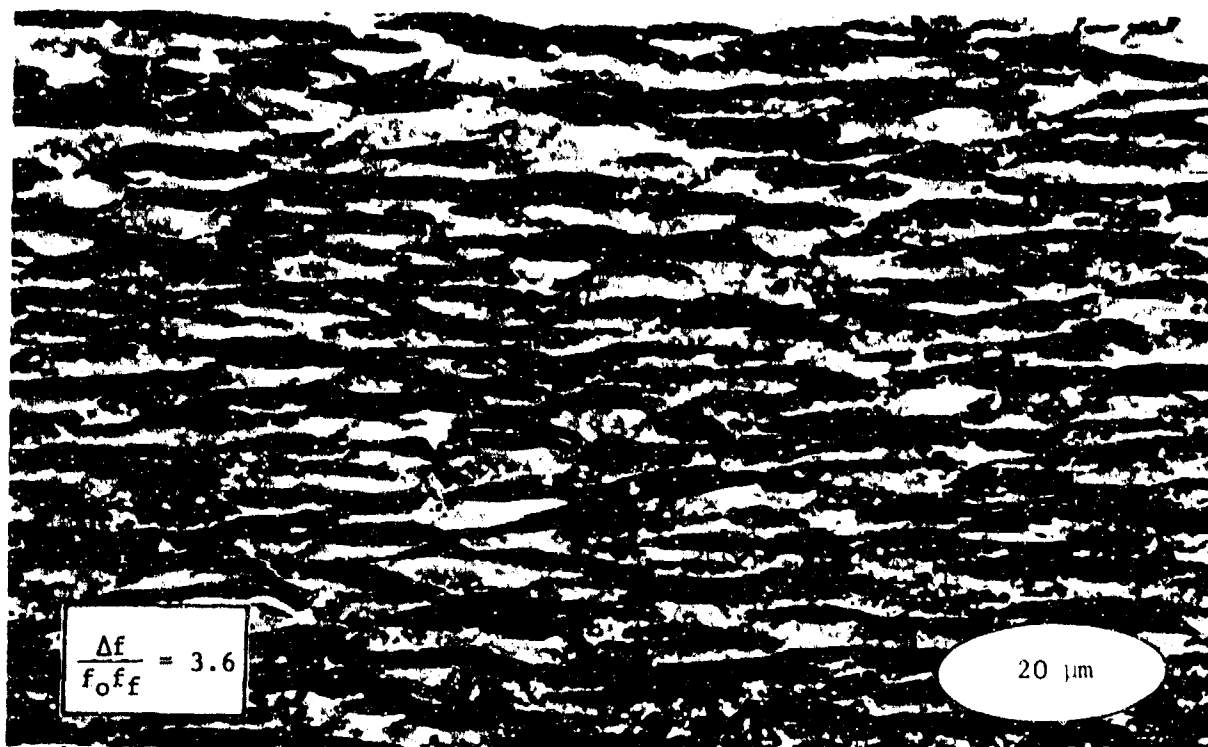
Figure 11.   Surface Etched to $\Delta f = 3.6 f_o f_f$.

$$\frac{\Delta f}{f_o f_f} = 8.9$$

20 μm

Figure 12.   Surface Etched to $\Delta f = 8.9 f_o f_f$.

14

Figure 13. Surface Etched to $\Delta f = 31.5 f_o f_f$.

Figure 14. Surface Etched to $\Delta f = 85 f_o f_f$.

15

The surface roughnesses and roughness angles of both the 12 µm and 3 µm lapped groups leveled off after a depth of etch of approximately $\Delta f \simeq 80 f_0 f_f$, as shown in Figures 15 and 16. The equilibrium surface roughnesses are 0.45 µm and 0.075 µm; the equilibrium roughness angles are 0.75° and 0.25°, respectively. The ratios of the equilibrium values for these two groups are of the same order as the ratios of the average particle sizes of the two abrasives used in the final lapping.
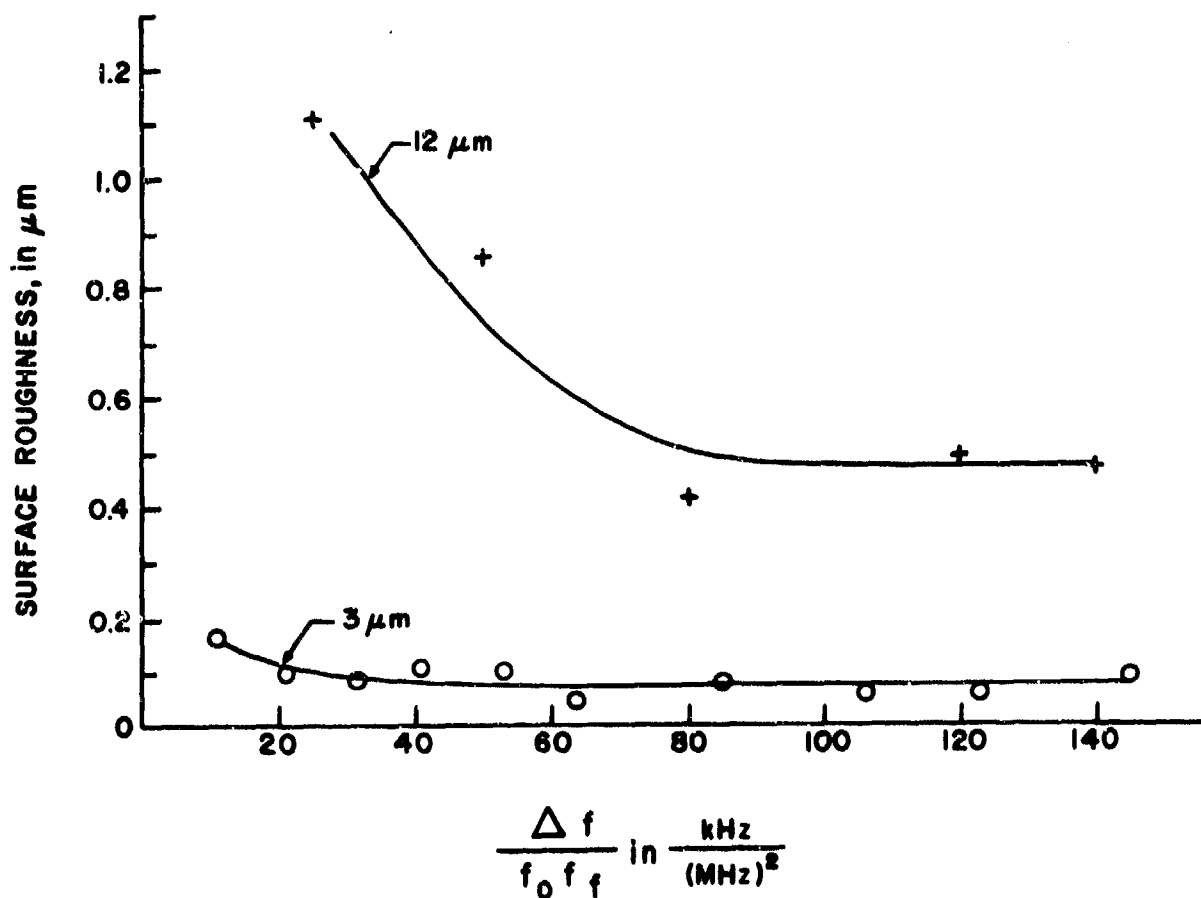
Figure 15. Surface Roughness vs. Depth of Etching for 3 µm and 12 µm Lapped Blanks.

ROUGHNESS ANGLE, in degrees

3.0

2.5

12 μm

2.0

1.5

3μm

1.0

0.5

0

20   40   60   80   100   120   140

$$\frac{\Delta f}{f_o f_f} \quad in \quad \frac{kHz}{(MHz)^2}$$
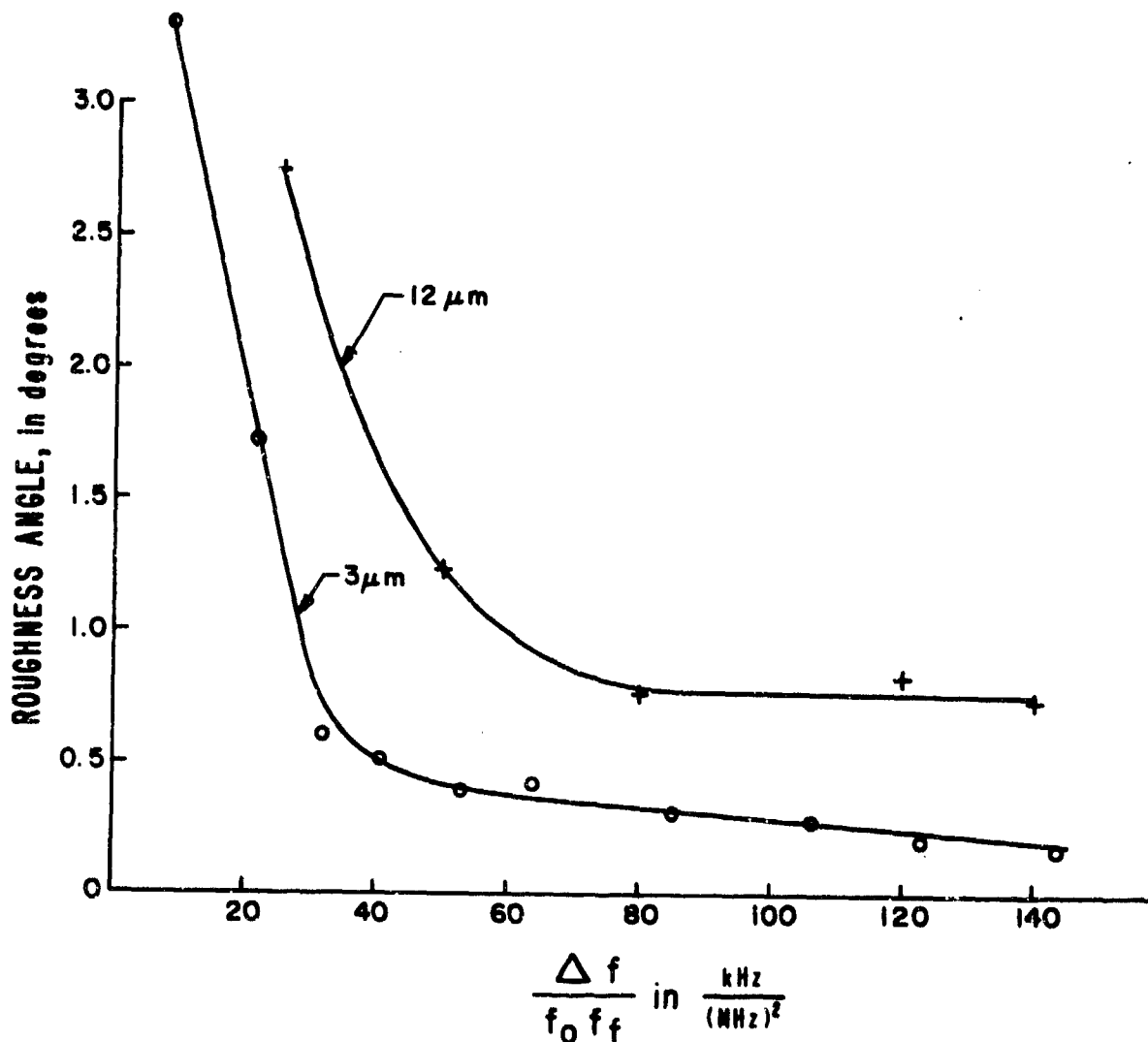
Figure 16.   Roughness Angle vs. Depth of Etching for
3 μm and 12 μm Lapped Blanks.

   The regular array of hills and valleys which developed on the lapped
blanks did not develop on the group of polished blanks. The equilibrium
topographies on these blanks consisted of smooth areas and scratch marks only.
Figure 17 shows the profile meter scan for a polished blank after it was
etched to $\Delta f = 92 f_o f_f$. It shows a 0.28 μm deep scratch mark, plus some
smaller ones. However, between the scratch marks, the surface is smooth, to
within the resolution of the profile meter which is 0.01 μm.

   These results are consistent with the contention that the etching is
diffusion controlled. The rougher the initial surface, the rougher the final
equilibrium surface, where the depleted surface layer of etching solution has

17

Figure 17. Profile Meter Scan of Polished Blank
after Etching to $\Delta f = 92f_0f_f$.

uniform thickness everywhere, and the hills, therefore, are no longer etched
faster than the valleys. A smooth, undisturbed initial surface remains
smooth even after a large amount of material is removed by the etching. No
signs of preferential etching along the different crystallographic axes
appeared on the polished blanks.

The scratch marks represent lattice disturbances which had been produced
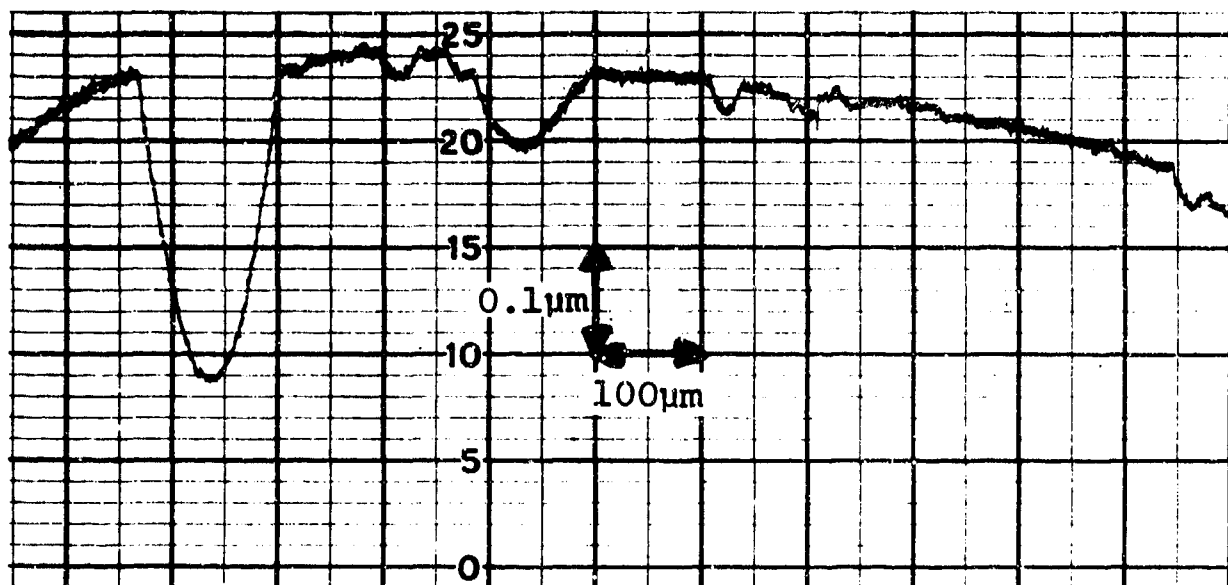by the mechanical polishing operation. The reason these regions are etched
faster than the surrounding areas is the same as the reason for the formation
of etch pits and etch channels, which will be discussed later in this report.

The results above for the 12 μm and 3 μm lapped surfaces are not
necessarily representative of surfaces lapped with the same size-designation
abrasives from different manufacturers. The typical size-distribution curves
for the 12 μm and 3 μm MICROGRIT WCA abrasives show the median particle
diameters to be 11.75 μm and 2.85 μm, respectively, and the maximum particle
diameters to be approximately 30 μm and 10 μm, respectively.[17] The particles
tend to have flat, platelet-like shapes. Figure 18 shows an SEM micrograph
of some 3 μm suspension-treated MICROGRIT WCA particles. Abrasives from
other manufacturers may have different particle size distributions and/or
shapes and may therefore produce different equilibrium surface topographies
upon chemical polishing.

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17. The particle size analysis was performed on a Coulter Counter, Model T,
    Coulter Electronics Inc., 540 W. 20th St., Hialeah, FL 33010--data
    supplied by Micro Abrasives Corp.--see Ref. No. 7.

Figure 18.   3 μm MICROGRIT Abrasive.

   The above results imply that the less deeply and the more uniformly dis-
turbed the surface is prior to etching, the smoother will be the chemically
polished surface. Accordingly, one should lap with as fine an abrasive as
possible prior to etching. Since the finer the abrasive, the slower the lap-
ping, it may be preferable to perform the chemical polishing in two steps in
order to attain the optimum surface finish. First, lap the crystals with a
relatively coarse abrasive, e.g., 3 μm; then etch to $\Delta f \simeq 10 f_o f_f$ to remove the
damaged layer and chemically polish the surface. At this point the (r.m.s.)
surface roughness is 0.11 μm, and the profile meter scans show that the
largest hills on the surface (if the surface is free of etch channels) extend
less than 0.5 μm above the valleys. To produce a semi-polished surface, it is
therefore sufficient to remove $\Delta f \simeq 0.3 f^2$ with a fine abrasive. From such a
semi-polished surface, a small amount of etching should produce a very smooth
chemically polished surface.

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In our experience, etching surfaces which had been fully polished with cerium oxide prior to etching have generally produced scratch marks. Although the above suggestion for using a semi-polished surface for chemical polishing has not yet been proven experimentally, the semi-polished surface may be preferable to a fully polished one, because rather than aiming for a perfectly scratch-free surface, lapping with a fine abrasive produces a uniformly "scratched" surface similar to the ones produced by the 12 μm and 3 μm abrasives, except on a smaller scale.

c. Temperature: The temperature at which the etching is performed does not have a significant effect on the final surface roughness in the temperature range studied, $45°C$ to $90°C$. The temperature does, however, have a significant effect on the rate of etching. Figure 7 shows a semi-log plot of the temperature dependence of etch rate in saturated ammonium bifluoride. (Note the temperature scale in $°C$ at the top of the graph.) The rate increases from $\Delta f = 0.063 f_o f_f$ per minute at $45°C$ to $\Delta f = 1.1 f_o f_f$ per minute at $90°C$. It is $1 f_o f_f$ per minute at $88°C$, which implies that from a 3 μm surface, a chemically polished surface can be produced at this temperature in less than 15 minutes. The etch rate curve in Figure 7 fits the equation

$$R(T) = Ae^{-\frac{E}{kT}} \tag{1}$$

where $R(T)$ is the etch rate in units of kHz per $(MHz)^2$ per minute,

$$A = 5.083 \times 10^8 \times \Delta f / (f_o f_f \text{ min}), \tag{2}$$

$$E = 14.4 \text{ kcal/mol} (=0.62 \text{eV}), \tag{3}$$

k is Boltzmann's constant, and T is the temperature in $°K$. All etch rates are the rates for chemically polished surfaces. (The initial etch rates on rough surfaces are always higher.)

The 14.4 kcal/mol activation energy is higher than the activation energies characteristic of diffusion controlled processes,[6] which are 4 to 6 kcal/mol. The simple expression above, however, does not take into account two effects. First, the etching solution is saturated at all temperatures, which means that the concentration increases with increasing temperature. Secondly, the etching reaction liberates heat which makes the temperatures at which the reaction takes place higher than the bulk solution temperature.

Both of these effects tend to change the apparent activation energy to a value which is higher than the "true" activation energy of the etching.

d. Agitation: The agitation rate has only a minor effect on the etch rate. For example, the etch rate with an agitation rate of 50 cycles per minute was compared with the etch rate with no agitation, at $85°C$. A group of crystals was etched in 15-minute increments, alternating between agitation and no agitation. The etch rates were found to be 11% higher during the agitation periods.

Such a change in etch rate at $85°C$ could be accounted for by a change in etchant temperature of only $2°C$, which is close to the uncertainty in our temperature control. This uncertainty in temperature control could therefore possibly account for at least part of the observed increase in etch rate.

While agitation does not appear to have a significant effect on the etch rate, proper agitation, preferably in both directions, is important to assure that the crystals are etched uniformly on both sides. Agitation also serves to minimize temperature gradients in the etch bath, which in turn minimizes the blank-to-blank etch rate variations.

e. <u>Etch bath depletion</u>: To obtain an indication of the effects of a severe depletion of the etch bath, a handful (approximately 40 grams) of crystal blanks were dissolved completely in approximately 200 ml of etching solution. This is equivalent to the depletion that would be produced in a one-liter etch bath by etching 100,000 blanks of 6.4 mm diameter to $\Delta f = 14 f_0 f_f$. The "depleted" etch bath contained enough $NH_4F \cdot HF$ flakes to assure that some undissolved flakes remained on the bottom of the bath after all the crystal blanks had dissolved.

A group of blanks was then etched in this bath from 14.8 MHz to 20.0 MHz $(\Delta f/(f_0 f_f)) = 17.6)$ at 53°C. SEM photos of the etched surfaces revealed no difference between these surfaces and surfaces etched the same amount in a fresh etching bath. The etching rate in the depleted etch bath, however, was lower by a factor of seven.

No attempt was made to chemically analyze the depleted etch bath. Judge[18] has, however, examined by Raman spectroscopy a solution of NH_4F and HF ("7:1 buffered HF") before and after dissolving SiO_2 in it. The "before" solution showed no detectable absorptions. In the spectrum of the solution with SiO_2 dissolved in it, "a very large number of peaks are observed, indicating the presence of multiple product species." The lower etch rate in the "depleted" etch bath is probably due to the presence of a high concentration of these species.

f. <u>Quality of quartz--natural vs. cultured</u>: At the completion of chemical polishing, the blanks are inspected for etch pits and etch channels using the technique described earlier. At the two points where an etch channel intersects the blank surfaces, etch pits have always been found; however, the etch pits are not always associated with etch channels. Although the effects of etch pits and etch channels on resonator performance have not yet been determined, we are currently rejecting all blanks with etch channels. There are primarily two reasons for this. First, the etch channels are probably filled with ammonium bifluoride at the completion of etching. Rinsing the blanks will almost certainly fail to remove all of the fluorides from the channels. The presence of fluorides in the etch channels, therefore, is likely to adversely affect the resonator's stability. Since the etch rate through the etch channels can be about 100 times as high as through the rest of the blank, even lightly etched blanks may contain channels which extend at least part way into the blanks.

18. Judge, J. S., "A Study of the Dissolution of SiO_2 in Acidic Fluoride Solutions," J. Electrochem. Soc., Vol. 118, pp. 1772-1775, November 1971.

The second reason is that the inspection for etch channels can be per-
formed early in the resonator fabrication sequence. For example, in the fab-
rication of circular resonators, a deep etch and inspection for channels can
follow the rounding operation, at which point the cost of a blank is still
relatively small. The deep etch at that point can also serve to prepare the
blanks for fine lapping by removing material from the blanks rapidly, con-
veniently, without angle change, and without producing any surface damage
(in fact, the deep etch removes the surface damage left by the previous
abrasive).

Since the institution of the deep etch followed by inspection as part of
our resonator fabrication process, we have inspected well over one thousand
natural quartz blanks, in several lots. The blanks were 6.4 mm diameter and
were intended for being made into 20 MHz fundamental resonators. The inci-
dence of etch channels in these 6.4 mm diameter blanks was between 30% and
40%; i.e., in each lot, 60% to 70% of the blanks were free of etch channels.
In larger diameter blanks, of course, the incidence of etch channels is higher.

When the chemical polishing was attempted on a group of cultured quartz
blanks, the resulting surfaces appeared to the unaided eye to be unevenly
etched. A closer examination of the surfaces revealed that the poor chemical
polish was due to a very large number of etch pits on the surfaces, most of
which were the terminations of etch channels. Figures 19, 20, and 21 show
SEM micrographs at different magnifications of one such surface showing the
etch pits and etch channels. None of the blanks in this group were free of
etch channels.

To investigate how the different varieties of cultured quartz compare
with natural quartz with respect to the incidence of etch channels, sixteen
varieties of cultured quartz from ten different growers were deeply etched and
inspected for etch channels. Three of the varieties were swept quartz.

The sixteen varieties could be divided into three categories. One
variety, a swept quartz, was free of etch channels. Five varieties had only a
few etch channels per blank--on the order of 10 channels per cm^2 of blank
surface. The two remaining swept varieties were in this second category.
Figure 22 shows a light micrograph of how such a blank appears during inspec-
tion with edge illumination. The remaining ten varieties contained a large
number of etch channels per cm^2. Inspection of blanks from the worst varieties
in this group is comparable to observing the Milky Way at night, as shown in
Figure 23.

The one variety which was free of etch channels was vacuum swept at Sandia
Laboratories by a process similar to that described by King.[19] Some of the
effects of sweeping in vacuum, as opposed to sweeping in other atmospheres,
has also been discussed by Krefft,[20]

19. King, J. C., "Vacuum Electrolysis of Quartz," US Patent No. 3,932,777,
    Jan. 13, 1976.

20. Krefft, G. B., "Effects of High Temperature Electrolysis on the Coloration
    Characteristics and OH-Absorption Bands in Alpha-Quartz," Radiation
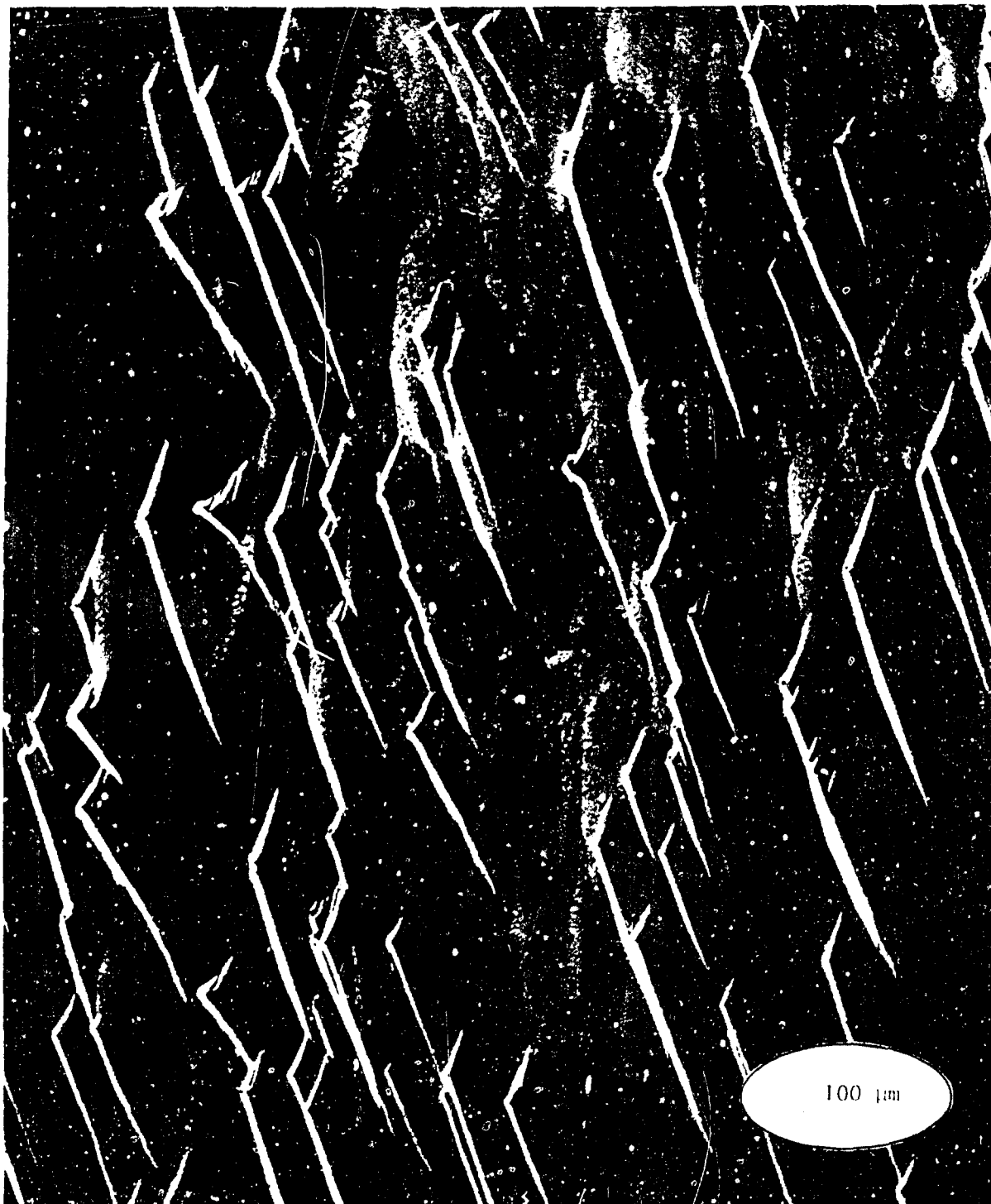   Effects, Vol. 26, pp. 249-259 (1975).

100 μm

Figure 19.   A Cultured Quartz Blank after Etching

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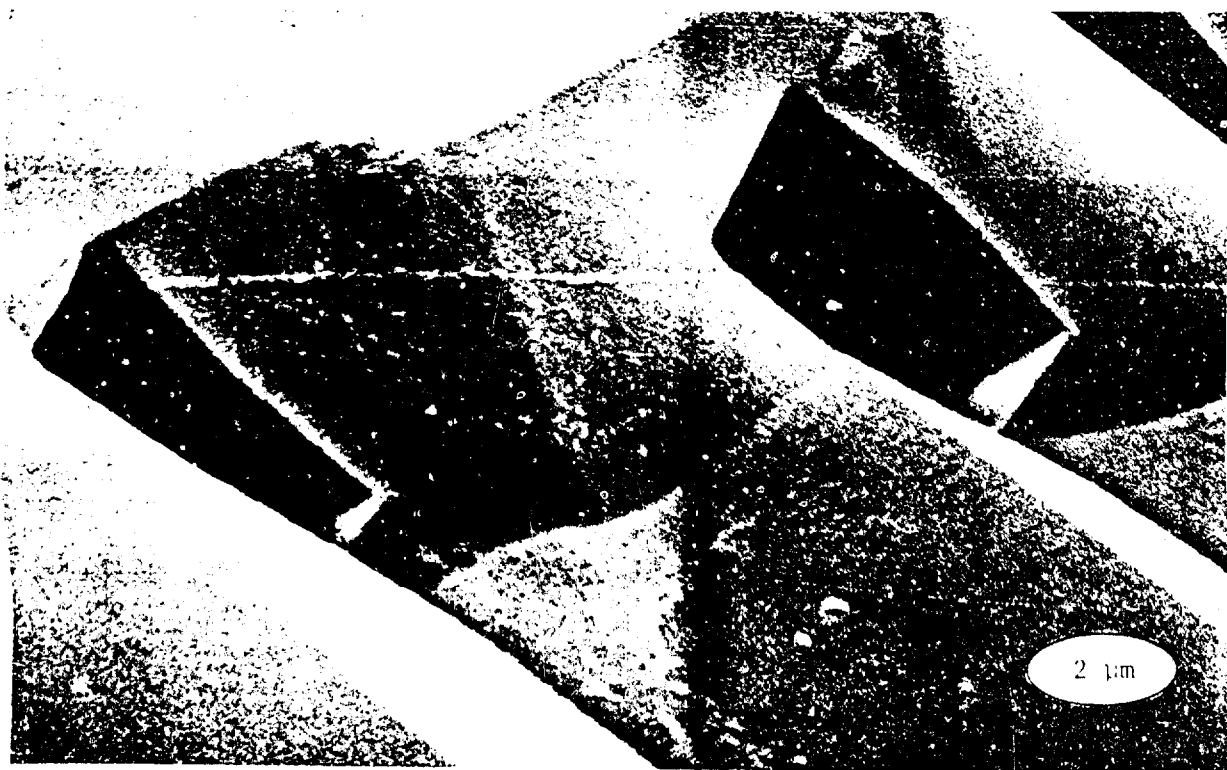Figure 20.   Etch Pits and Etch Channels in Deeply Etched Cultured Quartz.

2 µm

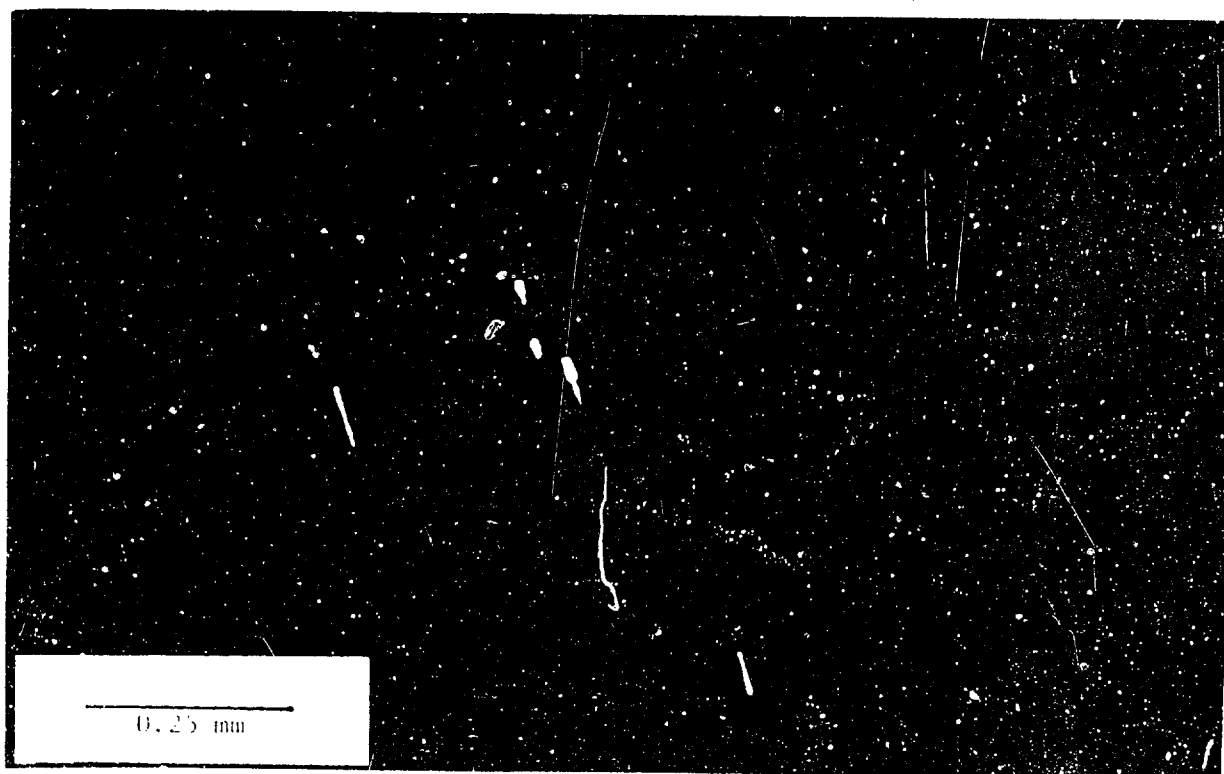Figure 21.   Etch Channels at the Bottom of Etch Pits.

0.25 mm

Figure 22.   Etch Channels Observed under a Microscope
with Edge Illumination.

25
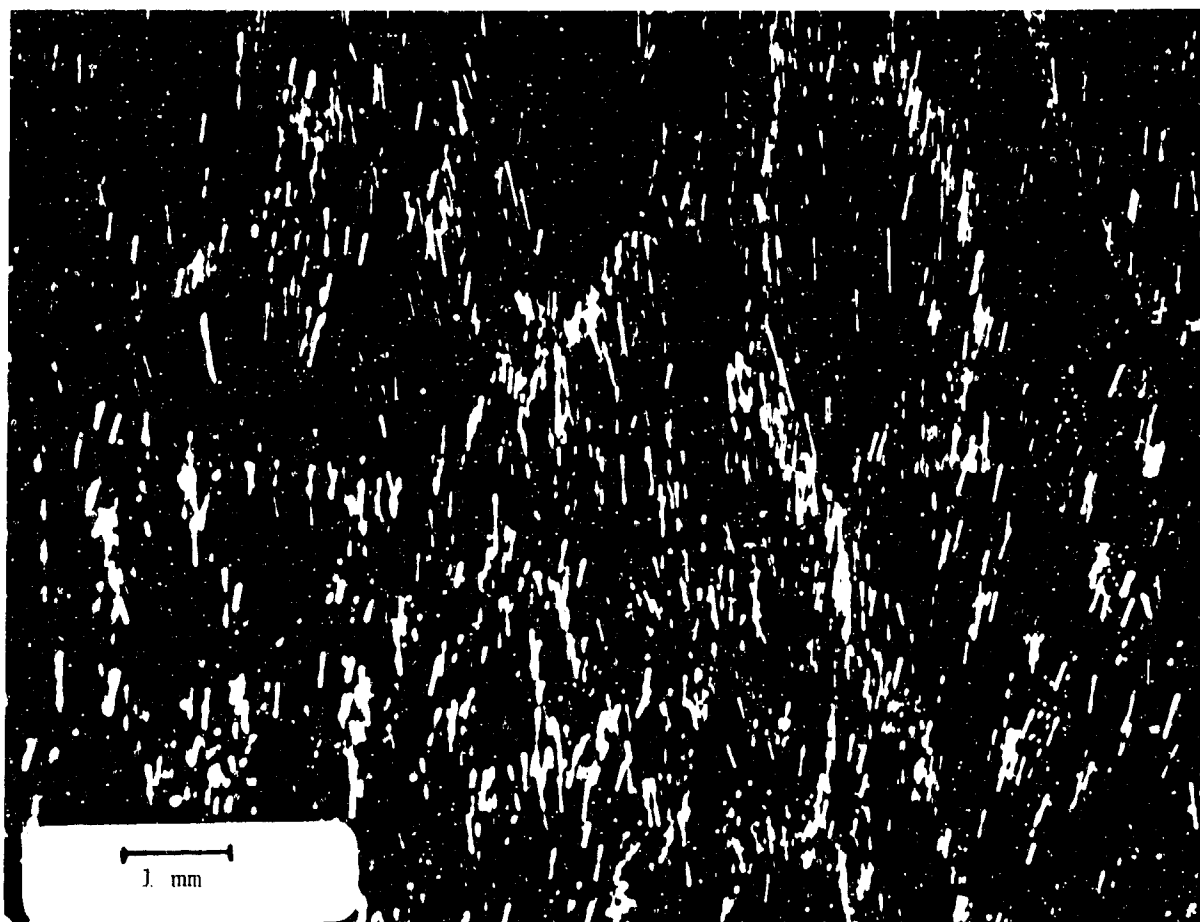
Figure 23. Etch Channels in a Blank Made of
Poor Quality Cultured Quartz.

and by King and Sander,[21] who showed that resonators made from vacuum-swept
cultured quartz exhibited much lower frequency offsets after burst irradiation
than resonators made from natural quartz or air-swept cultured quartz.

We were able to obtain a few blanks from both the vacuum-swept and
unswept portions of the same bar of cultured quartz. Whereas the blanks from
the swept portion were completely free of etch channels (three blanks were
etched, each 15 mm in diameter), the blanks from the unswept portion contained
numerous etch channels. Figure 24 shows a side-by-side comparison of the

21. King, J. C., and Sander, H. H., "Transient Change in Q and Frequency of
     AT-cut Quartz Resonators Following Exposure to Pulse X-rays," IEEE Trans.
     on Nuclear Science, Vol. NS-20, pp. 117-125 (1973).

swept and unswept blanks as they appeared under the microscope with edge illumination. Even after the swept blanks were etched further, until a total of 300 µm was removed in an 85°C etch bath, not a single etch channel was observable. There were, however, several etch pits visible on each of the surfaces. The number of etch pits on the vacuum-swept blanks appeared to be fewer than on the unswept blanks, although the sample sizes were not large enough to allow us to draw a definite conclusion about this, especially since there were areas on both types of blanks which were free of etch pits.
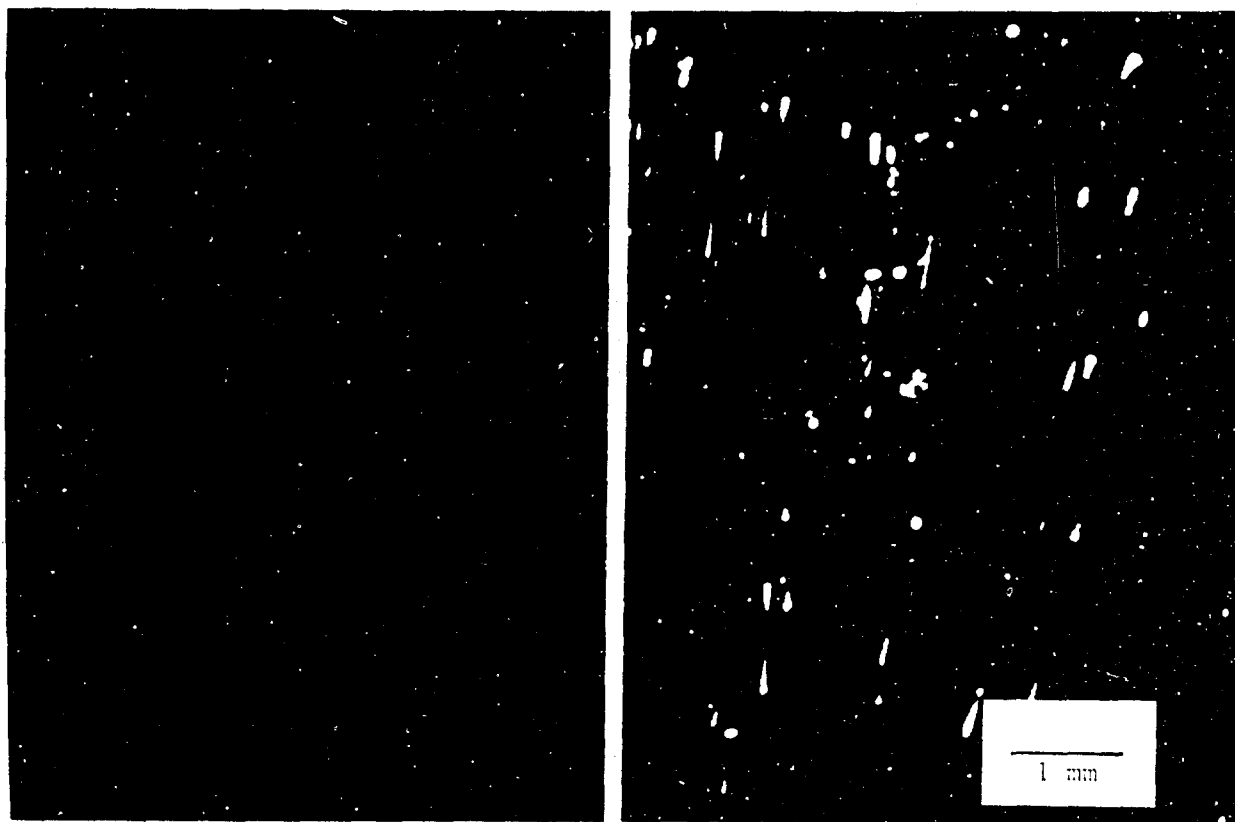

Figure 24. Vacuum Swept vs. Unswept Blanks from the Same Bar of Cultured Quartz.

Etch channels in quartz have been observed previously.[22-29]* They are probably a consequence of dislocations at which impurities had segregated.[6,22] Impurities dissolved in the quartz, particularly those which do not fit into the lattice, segregate at dislocations. There is a strain energy associated with the presence of these impurities which results in the dislocations being etched more readily than the rest of the surface; i.e., the activation energy for etching is reduced by the strain energy. The dislocation may also act as a point of nucleation of attack. In such a case, when there is also a considerable heat of reaction, the heat generated can enhance both the diffusion and the rate of reaction in the vicinity of the dislocation, which can result in an etch channel and/or etch pit being formed. Figure 25 shows an SEM micrograph of etch pits on the surface of a deeply etched ($\Delta f \simeq 85 f_o f_f$) natural quartz blank. In natural quartz, some of the etch channels may be due to fission tracks.[30]*

Sweeping is known to be able to remove interstitial impurities from quartz. The low incidence of etch channels in the three swept quartz varieties is probably due to the relief of the strain energy associated with these impurities. The difference in the incidence of etch channels between the vacuum-swept quartz and the other two swept varieties (which were swept in air) may possibly be accounted for by the fact that when sweeping takes place in air, as the impurities in the crystal diffuse toward the cathode, impurities from the air can diffuse into the crystal from the anode side.[20]

The presence of etch channels also seems to be associated with an apparent increase in the etch rate of quartz. A group of natural quartz and a group of one of the better quality cultured quartz blanks were etched and inspected for channels. From the group of natural quartz blanks, the ones with etch channels were eliminated. The cultured quartz blanks were 7.6 mm diameter and contained about ten channels per blank. The two groups of blanks were etched simultaneously side by side, in the same etch bath, at 85°C. The rate of etching was measured, as usual, by measuring $\frac{\Delta f}{f_o f_f}$ per minute.

It was found that the etch rate for the cultured quartz group was 1.6% higher. When the experiment was repeated with a group of natural quartz blanks without any etch channels and a group of poor quality ("Milky Way-like") quartz, the etch rate of the "Milky Way" quartz was found to be 4.9% higher. When two groups of natural quartz blanks were etched side by side, although the groups had been obtained from different suppliers and had different initial surface finishes (12 μm vs. 3 μm), different frequencies (6.5 MHz vs. 5 MHz), and different geometries (circular vs. square), the average etch rates for the two groups differed by less than 0.2% (although blank-to-blank etch rate variations larger than 0.2% were observed in each of the two groups). All etch rates were measured after the blanks had been chemically polished.

30. Macdougall, J. D., "Fission--Track Dating," Scientific American, Vol. 235, pp. 114-122, December 1976.
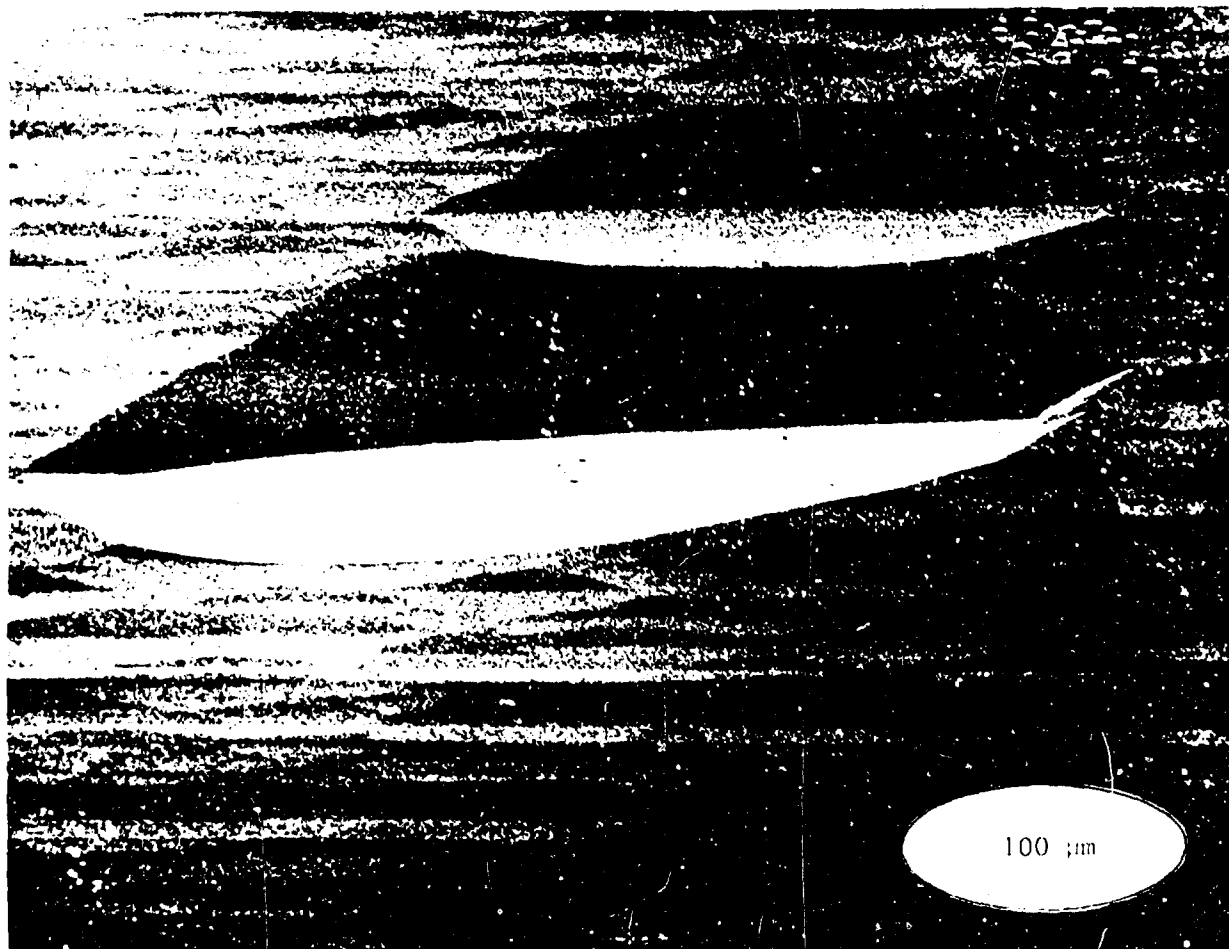
Figure 25.   Etch Pit in a Deeply Etched Natural Quartz Blank.

THE STRENGTHS OF CHEMICALLY POLISHED BLANKS

The theoretical inherent strengths of elastic materials are generally
orders of magnitude greater than the measured strengths of the ordinary forms
of these materials. This reduction in strength is known to be caused princi-
pally by surface flaws, such as scratches, which concentrate the applied
stress and thereby lead to fracture at loads which are much lower than the
theoretical maximum. Removal of all flaws from the surface permit the
strengths of materials to approach the theoretical maximum. For example,[31]
the theoretical strength of fused quartz (and of other glasses) is about
1.8×10^{10} Pa. The actual strengths measured are in the range of 10^7 to
10^8 Pa. However, by heating glasses to above their softening point (i.e.,
fire polishing) the surface flaws can be eliminated. The strength of fire

31.   Doremus, R. H., "Glass Science," New York: John Wiley & Sons. Inc.,
      Chapters 15 and 17   (1973).

polished fused quartz has been measured to be as high as 1.5×10^{10} Pa, nearly as high as the theoretical maximum.

Since the surfaces of chemically polished quartz blanks appear to be free of surface damage, an experiment was performed to determine how the strengths of these blanks compare with the strengths of mechanically polished blanks and with the strengths of lapped blanks. The experiment consisted of supporting the blanks only at the edge, placing a spherical indenter at the center of the blank, gradually increasing the load on the indenter, and measuring the load required to fracture the blank. A photograph of the apparatus, together with a sketch of the area where the indenter contacts the blank, is shown in Figure 26. The indenter was a steel ball which was connected by means of a shaft to a platform on which a 2000 ml plastic beaker could be placed. The blank was supported by a 0.5 mm wide rim made of a hard plastic.
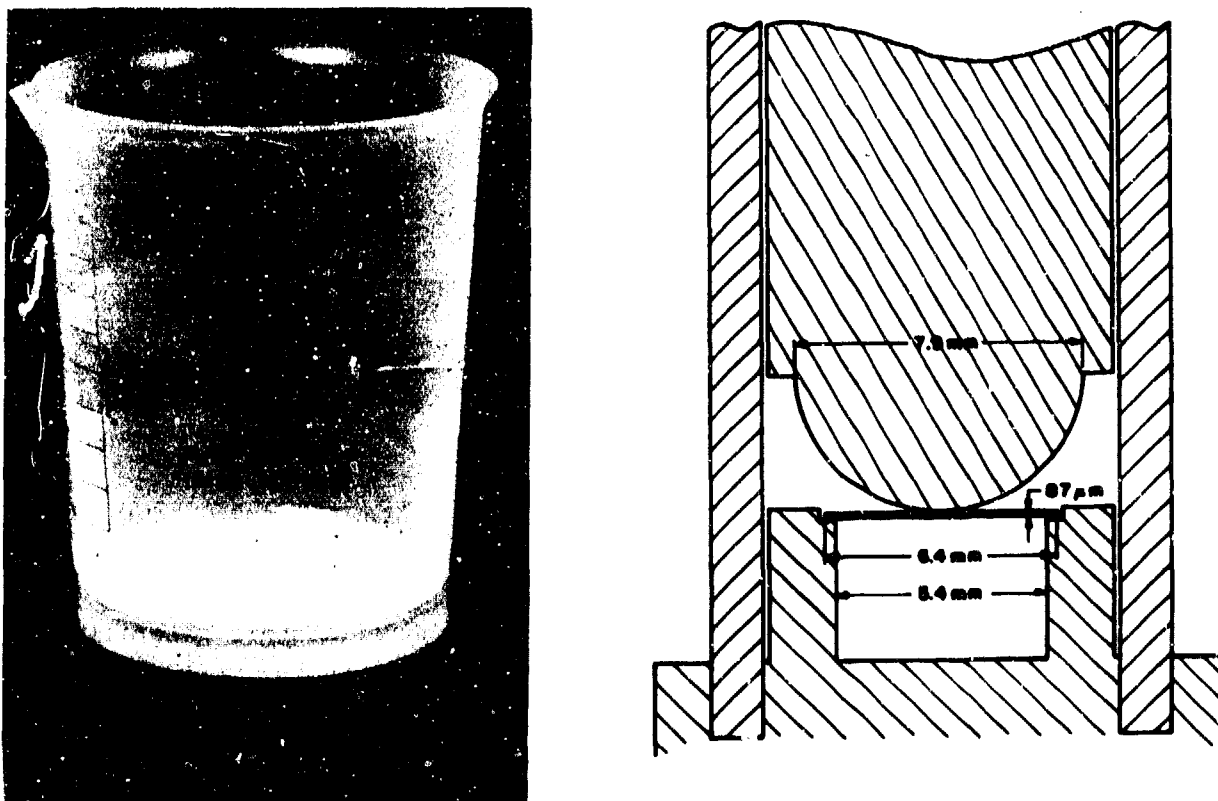

Figure 26. Apparatus for Blank Strength Evaluation.

A group of twelve 20 MHz, 6.4 mm diameter AT-cut blanks were tested. The blanks had been etched $15f_o f_f$, from a 3 μm lapped initial surface. The average load on the indenter at breakage was 2.2 kg. Two of the blanks did not break when the beaker was overflowing with water--a load of 3.1 kg.

(These numbers should be considered to be only a semi-quantitative indication of the inherent strength of these blanks because, for example, each time a blank fractured, the rim on which the blanks were supported was damaged. The load on the next blank, therefore, may not have been as uniformly distributed.)

It was not possible with this apparatus to measure the strengths of blanks of the same dimensions which had been mechanically polished or lapped with 3 μm abrasive, because all such blanks broke under the weight of the platform alone (i.e., without the beaker)--a weight of 157 grams.

To place the strength of the chemically polished blanks in perspective, consider the fact that the weight of a 20 MHz blank of 6.4 mm diameter is only 7.0 mg; i.e., the ratio between the average load on the indenter at breakage and weight of the blank is about 300,000. This also means that the shock level, at which the load on the blank due to its own weight is equal to the average load on the indenter at breakage, is 300,000g.

To obtain a rough approximation of the shock levels the 20 MHz fundamental chemically polished blanks can survive when supported by four point mounts, the rim on which the blanks were supported was reduced to four small areas 90° apart. The dimensions of each area were 0.5 mm in the radial direction and 0.4 mm in the tangential direction. The average load on the indenter at breakage was thus reduced to 550 grams, which corresponds to a load due to a shock of about 80,000g.

An additional indication of the high resistance to fracture in these chemically polished blanks is that when some 14 mm diameter blanks were etched from 15 MHz to above 120 MHz, the blanks flexed like very thin sheets of mica. For example, holding such a blank at diametrically opposite points between two fingers, the blank could be bent about 90° before it broke.

THE Q OF CHEMICALLY POLISHED RESONATORS

The Q of a resonator can be defined by

$$Q = 2\pi \frac{\text{Energy Stored}}{\text{Energy Dissipated per Cycle}}$$

The energy dissipated per cycle is the sum of the energies dissipated by the various loss mechanisms. For a chemically polished resonator, the losses may be due to: the mounting, the bonding, the electrodes, contamination, the atmosphere surrounding the resonator, the intrinsic losses in the quartz, plus the losses due to the features produced by chemical polishing, i.e., the regular array of hills and valleys, the etch channels, and the etch pits. Q^{-1} can therefore be expressed as the sum of the Q^{-1}'s due to the various loss mechanisms, i.e.,

$$\frac{1}{Q} = \frac{1}{Q_{mounting}} + \frac{1}{Q_{bonding}} + \ldots + \frac{1}{Q_{etch\ pits}}$$

If the regular array of hills and valleys due to chemical polishing produces an inherent Q degradation, then in a group of resonators made from blanks which received the same chemical polishing, the resonator with the highest Q represents a lower limit on the Q achievable with that chemical polish (at the given frequency).

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Since these investigations on chemical polishing began, we have fabricated approximately 300 resonators using chemically polished blanks. All of the resonators were fundamental mode, in the 18 MHz to 22 MHz range. The blanks were plano-plano, 6.4 mm diameter natural quartz. Most of the resonators were of the high shock, nickel electrobonded type described previously.[32] The depths of etch ranged from $\Delta f = 2f_o f_f$ to $\Delta f = 22f_o f_f$. The surfaces had been lapped with 3 μm MICROGRIT prior to etching. For the highest Q resonators in each group, the motional capacitances ranged from 12 fF to 13.5 fF; the resistances ranged from 3 Ω to 5 Ω; and the Q's thus ranged from 140,000 to 210,000, with no apparent Q degradation with depth of etch.

The highest Q resonators made from polished blanks of the same blank geometry, but of a low shock nickel electrobonded design,[33] had Q's which were no higher (Q $\simeq$ 180,000) than the highest Q resonators made from chemically polished blanks. In fact, the highest Q resonator of that blank geometry we have made to date (Q $\simeq$ 210,000) was a 19 MHz high shock resonator, with a depth of etch of $\Delta f = 16f_o f_f$.

In an attempt to investigate the effect of an extreme amount of etching, a group of crystal blanks were etched from 10.5 MHz to 22.4 MHz, which corresponds to a $\Delta f = 50f_o f_f$. Prior to etching, these blanks had been in process to be made into 20 MHz resonators. Normally, the blanks would have been lapped to at least 15 MHz with 3 μm MICROGRIT before being etched to the final frequency. Although the 10.5 MHz blanks were lapped with the 3 μm abrasive, the amount of material removed with this abrasive was much less than usual, and the surface finish prior to etching may not have been a true 3 μm finish.

The highest Q resonator in this group (of eleven resonators) had a Q of 110,000 (C_1 = 13.4 fF, R = 5 Ω). Most of the resonators in this group had anomalously low C_1's, the cause of which has not yet been determined. This experiment did show, however, that if the extremely deep etching produces a Q degradation, this degradation is not a drastic one--at least not for fundamental mode resonators in the 20 MHz range. The Q's of the above resonators were not evaluated on overtone operation because the electrodes were gold, with about a 1.0 f^2 plateback, which is known to be too heavy for overtone operation.[34]

32. Filler, R. L. and Vig, J. R., "The Effect of Bonding on the Frequency vs. Temperature Characteristics of AT-cut Resonators," Proc. of the 30th Annual Symposium on Frequency Control, US Army Electronics Command, Ft. Monmouth, NJ, pp. 264-268 (1976). Copies available from Electronics Industries Assoc., 2001 Eye Street, NW, Washington, DC 20006; also available as AD A030316.

33. Vig, J. R., LeBus, J. W., and Filler, R. L., "Further Results on UV Cleaning and Ni Electrobonding," Proc. of the 29th Annual Symposium on Frequency Control, US Army Electronics Command, Ft. Monmouth, NJ, pp. 220-229 (1975). Copies available from EIA, as in Ref. 32.

34. Bennett, R. E., editor, "Quartz Resonator Handbook." Union Thermoelectric Div., 1960, pp. 113-115. Copies available from NTIS, AD 251289.

As the frequency increases so that the wavelength of the acoustic wave approaches the dimensions of the etch features, it would not be surprising to find a Q degradation. However, in any systematic study of the inherent Q degradation due to the array of hills and valleys which develop during chemical polishing, great care would have to be taken to use only those blanks which are free of both etch channels and etch pits, since the dimensions of these features are usually at least an order of magnitude larger than the dimensions of the hills and valleys. In the above resonators, the blanks selected were free of etch channels but not necessarily of etch pits.

CONCLUSIONS

Etching in a saturated solution of ammonium bifluoride has been shown to be capable of chemically polishing AT-cut quartz over a broad range of conditions. The quality of surface finish which can be produced by this method depends primarily on the surface finish prior to etching, the depth of etch, and the quality of quartz used. The speed at which chemically polished surfaces can be produced depends primarily on the temperature of the etch bath. In an 88°C etch bath, for example, starting with 3 µm lapped blanks, chemically polished surfaces can be produced in less than 15 minutes. Depletion of the etch bath slows down the etching rate but does not affect the surface roughness.

The process can remove large amounts of material from lapped blanks while simultaneously producing an improved surface finish, without producing shifts in the angles of cut. The process can also produce blanks of great strength, which is particularly important for high shock applications.

Since depth of etch is not critical, the chemical polishing may allow manufacturers to stock lapped blanks at only a few frequencies at each commonly used angle of cut, then etch the blanks to the required frequencies as the need arises. The method may also permit the manufacturing of miniature contoured high frequency resonators, since such small diameter resonators can now be contoured at conventional frequencies, then etched up to high frequencies. If a masking material which is resistant to the etch solution can be found, the method may also permit the fabrication of high frequency resonators and filters with the inverted mesa structure.

Inspection of deeply etched blanks for etch channels is a simple screening technique which can reveal large differences among blanks made from different varieties of quartz. The incidence of etch channels has not yet been correlated with resonator performance parameters such as stability, Q, radiation hardness, etc. From indirect evidence, however, it seems probable that, everything else being equal, resonators made from blanks which are free of etch channels will perform better than those which show etch channels upon deep etching.

friends in the crystal industry who provided us with the samples of different varieties of cultured quartz. We are particularly grateful to Tom Young of Sandia Laboratories for supplying the vacuum-swept and unswept blanks from the same bar of cultured quartz.

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APPENDIX A

THE ETCH RATES OF QUARTZ

The table below shows the etch rates of AT-cut quartz as a function of temperature, T, in $^{\circ}C$, and as a function of blank frequency, f, in MHz. In each square, the larger number is the rate in kHz per minute; the smaller number in the upper right hand corner is the rate in kHz per 10 seconds. The table also shows the rate as a function of temperature in units of μm removed from the blank thickness per minute and also in units of $\dfrac{\Delta f}{f^2 \,(min)}$, where

Δf is in kHz and f is in MHz.

TABLE A-1. THE ETCH RATES OF QUARTZ

T \ f	1.0	3.3	5.0	10	15	20	30	f \ T	$\mu m/min$ *	$\dfrac{\Delta f}{f^2 (min)}$
60	0.032 / 0.193	0.35 / 2.1	0.80 / 4.8	3.2 / 19	7.2 / 43	13 / 77	29 / 174	60	0.32	0.193
65	0.043 / 0.255	0.46 / 2.7	1.1 / 6.4	4.3 / 26	9.5 / 57	17 / 102	38 / 230	65	0.42	0.255
70	0.060 / 0.36	0.65 / 3.9	1.5 / 9.0	6.0 / 36	14 / 81	24 / 144	54 / 324	70	0.60	0.36
75	0.078 / 0.47	0.85 / 5.1	2.0 / 11.8	7.8 / 47	18 / 106	31 / 188	71 / 423	75	0.78	0.47
80	0.11 / 0.65	1.2 / 7.1	2.7 / 16.3	11 / 65	24 / 146	43 / 260	98 / 585	80	1.08	0.65
85	0.14 / 0.85	1.5 / 9.2	3.5 / 21.3	14 / 85	32 / 191	57 / 340	128 / 765	85	1.41	0.85
90	0.18 / 1.10	2.0 / 12	4.6 / 27.5	18 / 110	41 / 248	73 / 440	165 / 990	90	1.83	1.10
T \ f	1.0	3.3	5.0	10	15	20	30	f \ T	$\mu m/min$	$\dfrac{\Delta f}{f^2 (min)}$

* μm/min REMOVED FROM THE BLANK THICKNESS

— kHz PER 10 SECONDS
— kHz PER MINUTE

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